*16th International Conference on Environmental Science and Technology*
*Rhodes, Greece, 4 to 7 September 2019*

# $TiO_2/CoFe_2O_4/Ag$ nanocomposites for photocatalytic reduction of water pollutants under UV and solar light

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## Abstract

Novel ternary catalysts $TiO_2/CoFe_2O_4/Ag$ with variable ferrite content were synthesized, characterized and used for the photocatalytic reduction of $Cr^{+6}$ pollutant, under UV and visible light illumination. Both $TiO_2$ and $CoFe_2O_4$ were synthesized using the sol-gel method followed by hydrothermal treatment to prepare $TiO_2/CoFe_2O_4$ (TCF) composite. Silver nanoparticles were successfully loaded on the surface of TCF to get three different composites, named as Ag/TCF. The crystal structure of the composites was analyzed by application of physicochemical characterization techniques. The presence of pure anatase phase $TiO_2$, cubic $CoFe_2O_4$, and silver nanoparticles was indicated in both XRD patterns and Raman spectra. It was found that the addition of silver nanoparticles has a great contribution to the photocatalytic reduction of $Cr^{+6}$ species. The photocatalytic reaction mechanism was studied by applying scavenging reaction process, revealing that electrons were strongly supported for the photocatalytic reduction of $Cr^{+6}$. After the photocatalytic experiments, the composite catalyst can be easily separated from the reaction solution by external magnetic bar and re-used.

**Keywords:** $TiO_2$ nanopowder; cubic $CoFe_2O_4$; titania / ferrite/silver composites; $Cr^{+6}$ photocatalytic reduction.

## 1. Introduction

Titanium dioxide is the most widely employed photocatalyst combining high activity under UV light irradiation with enhanced stability, low toxicity and low cost. For practical applications, there is a need to shift the photocatalytic response in the visible light domain, decrease the recombination of the photogenerated carriers and effectively remove the catalyst, after use. Recently, it has been shown that titania semiconductors can be effectively associated with cobalt ferrites (Ibrahim *et al.*, in press). The resulting nanocomposites present significant efficiency increase in the photocatalytic degradation of water pollutants caused by both iron and cobalt oxides in the complex matrix (Nazarkovsky *et al.*, 2016). And more important, they can be easily separeated from the reaction media by application of an external magnetic field. On the other hand, it is well known that deposition of noble metals like Ag, Au, Pt and Pd on the surface of $TiO_2$ enhances the photocatalytic efficiency under visible light by acting as an electron trap, promoting interfacial charge transfer and therefore delaying recombination of the electron–hole pair. In the case of silver, the visible light responsiveness of $TiO_2$ was accredited to the surface plasmon resonance of silver nanoparticles (Pelaez *et al.*, 2012). Thus in this work, ternary catalysts $TiO_2/CoFe_2O_4/Ag$ were synthesized, thorougly characterized and used with succes for the photocatalytic reduction of $Cr^{+6}$ species in water.

## 2. Results and Discussion

Titania and cobalt ferrite were prepared using sol-gel method, followed by hydrothermal process to prepare well-dispersed $TiO_2/CoFe_2O_4$ (TCF) composites. The silver coated TCF composites were prepared by an impregnation method. Fig. 1 presents the X-ray powder diffraction patterns of the photocatalysts. For titania, the pure anatase phase of tetragonal $TiO_2$ [space group I41/amd (141)] was identified, whereas for the titania/cobalt ferrite composite, the cubic spinel structure with Fd-3m (227) space group is also present. Silver loading results in the additional appearance of cubic silver [space group Fm-3m (225)]. The application of the Scherrer equation permits the calculation of the average crystal size of $TiO_2$ (26 nm), $CoFe_2O_4$ (107 nm) and Ag (12 nm), respectively. Moreover, Rietveld refinement gives the phase percentage (% w/w) for anatase (83.3), ferrite (9.89) and silver (6.84) components in the composite.

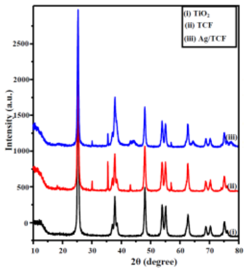

**Figure 1**. XRD patterns for $TiO_2$, TCF and Ag/TCF

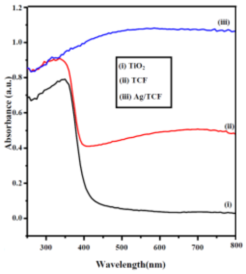

**Figure 2**. Corresponding UV-Vis spectra

The structural data were confirmed by Raman spectroscopy. In the corresponding spectra of the composites (not shown), the main characteristic vibration bands from both titania and ferrite components were observed. The existence of a red shift in the main $TiO_2$

vibration peak as well as the emergence of a low-frequency band are attributed to the presence of silver nanoparticles.

Further confirmation of the successful preparation of the composite photocatalysts was provided by the FT-IR spectra (not shown), presenting a broad absorption in the range of 462-580 $cm^{-1}$, resulting from a combination of the $TiO_2$ (Ti-O-Ti vibrations) and the spinel ferrite (stretching vibration of metal oxide in tetrahedral Fe(III)-$O^{2-}$ and stretching vibration in octahedral Co(II)-$O^{2-}$ group) peaks.

The optoelectronic properties of the photocatalysts were investigated by UV-vis spectroscopy (Fig 2). The main absorption of $TiO_2$ is below 410nm ($E_g$=3.1 eV) but the absorbance of the ferrites extends in the visible. The further absorbance increase in the visible domain for the Ag-TCF material is attributed to the surface plasmon resonance of Ag nanoparticle clusters.

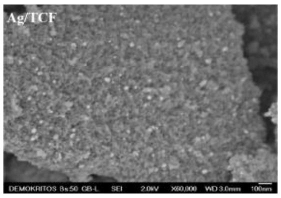

**Figure 3.** SEM image of the Ag/TCF composite photocatalyst

SEM analysis is in agreement with the above results. A characteristic SEM image for Ag/TCF (Fig. 3) indicates that the surface of the spinel (average size of about 138 nm) has been well-modified and decorated by the $TiO_2$ nanopowder (average particle size of 17 nm). The uniform formation of silver is clearly observed as bright particles with a slightly smaller size than that of pure $TiO_2$.

Fig. 4 (left and right) presents the photocatalytic reduction of $Cr^{+6}$ over $TiO_2$, TCF and Ag/TCF, under UV and visible light illumination, respectively. The results of the photocatalytic chromium reduction for all samples are summarized in Table 1.

**Table 1.** $Cr^{6+}$ photocatalytic reduction (UV and Day light)

| **Samples** | **Reduction efficiency (%)** | |
|---|---|---|
| | **UV light** (350-390 nm) 150 min | **Day light** (350-750 nm), 300min |
| **$TiO_2$** | 53.3 | 10.1 |
| **TCF** | 58.3 | 18.4 |
| **Ag/TCF** | 95.1 | 92.1 |

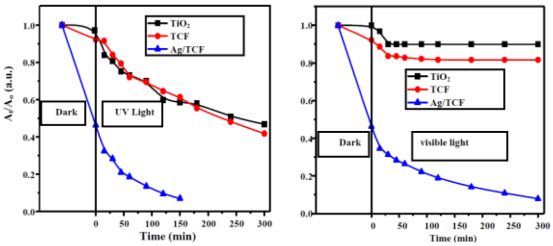

**Figure 4**. $Cr^{6+}$ reduction kinetics (UVlight, Day light) for $TiO_2$, TCF and Ag/TCF photocatalysts

Titania and ferrite alone or in combination present lower photocatalytic efficiency, comparing with the behaviour of Ag/TCF composite, thus confirming that silver nanoparticles play an important role, enhancing the photocatalytic reduction process. In fact, the highest $Cr^{+6}$ photocatalytic reduction was evidenced for Ag/TCF, under both UV and day (mainly visible) light illumination. This can be attributed to the high PZC, which increases the adsorption of $Cr^{+6}$ on Ag/TCF catalyst, via the electrostatic attraction between the photocatalyst and the cationic chromium species. Trapping experiments with scavengers were performed, under UV and visible light, to detect the reactive species and elucidate the photocatalytic reduction mechanism of the hexavalent chromium. It has been observed that the addition of isopropanol (IPA-hydroxyl radical scavenger) causes a small decrease in the photocatalytic reduction, under visible light and a small increase under UV irradiation, while benzoquinone (BQ-superoxide radical anion scavenger) and KI (hole scavenger) do not affect at all the reduction process. On the contrary, the addition of $KBrO_3$ (electron scavenger) leads to an inhibition of the photocatalytic reduction, under both UV and visible light. Thus, it can be concluded that the photogenerated electrons are the main active species in the photocatalytic reduction process.

The stability and reusability of the Ag/TCF composite was also examined and the rate constants remained unaffected, following five consecutive photocatalytic cycles under UV irradiation. Moreover, the XRD diffraction peaks of the composite remain unchanged after the fifth photocatalytic run, verifying the robustness of the new photocatalyst. And as the Ag/TCF composites present interesting magnetic properties, they were easily separated from the reaction solution using a magnet.

## Acknowledgements

This work was supported by the EC, Environment, LIFE17 ENV/GR/000387-PureAgroH2O Programme. P. Falaras also acknowledges funding from Prince Sultan Bin Abdulaziz International Prize for Water—Alternative Water Resources Prize 2014.

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